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METHOD OF CONVERTING HEAT ENERGY TO MECHANICAL ENERGY ON A RANKINE CYCLE

Abstract:

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DRAWINGS ATTACHED

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(54) METHOD OF CONVERTING HEAT ENERGY TO MECHANICAL ENERGY ON A RANKINE CYCLE

(71) We, MONSANTO COMPANY, a corporation organised under the laws of the State of Delaware, United States of America, of 800, North Lindbergh Boulevard, St. Louis 66, State of Missouri, United States of America, do hereby declare the invention for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

The present invention relates to a method for converting heat energy to mechanical energy. More specifically, it relates to the use of certain organic compounds which have been found to be of outstanding use in Rankine cycle equipment.

In a typical Rankine cycle power system, a suitable working fluid is passed in heat exchange relationship with a source of heat of sufficient intensity to vaporize the fluid. Thereupon, the energy of the expanding vapors is utilized to produce work by passing the vapors through a turbine or other work-producing device. The vapors are condensed and the condensed liquid is pumped back in heat exchange relationship with the heat source to complete the cycle.

Water or steam has been the most commercially utilized working fluid for Rankine cycle systems. The disadvantages of water or steam as a working fluid include those of high boiling point, high critical pressure and low density, all of which factors limit the power obtainable and result in the need for comparatively large and expensive apparatus. Furthermore, steam is deficient in entropy relationships along its saturated vapor line, showing an increasing entropy with decreasing pressure, and excessive condensation upon isentropic expansion. Accordingly, the use of a steam cycle normally requires superheating and resuperheating to prevent condensation of liquid in the turbine or other work-producing device, which liquid can cause erosion of metal and loss of efficiency. Unless provision is made for superheating, therefore, the expanded vapor may have an excessively high moisture content.

A variety of fluids have been evaluated in the past as working fluids for power cycles. Mercury is an example of such a fluid; however, the use of mercury in the Rankine cycle entails the disadvantage of high cost, and also that of exhibiting unfavorable entropy changes along the saturated vapor line. Furthermore, mercury is toxic and forms amalgams with certain metals.

The prior art has disclosed only a limited number of organic compounds as suitable working fluids for Rankine cycle use. Typical examples of prior art organic working fluids are biphenyl and the aliphatic fluorocarbons.

As efforts are made to reduce costs, improve operating efficiencies and reduce water consumption, the recovery and conversion to shaft power of waste heat from industrial process plants, chemical plants, oil refineries and prime movers such as gas turbines has become of considerable interest. Waste heat recovery systems based on the Rankine cycle, therefore, have many present day advantages and the thermal requirements for such systems have introduced a need for improved working fluids.

It has now been discovered that certain organic compounds can be advantageously employed as working fluids for Rankine cycle systems. These fluids are cycloaliphatic, heterocyclic or fused ring organic compounds and are characterized by having on a Mollier diagram a maximum entropy change between two established state points. According therefore to the present invention there is provided a method of converting heat energy to mechanical energy which comprises the steps of:

(a) vaporizing a fluid by passing the same in heat exchange relationship with a heat source, said fluid comprising an organic compound selected from cycloaliphatic, heterocyclic and fused ring organic compounds, and characterised by an entropy change not greater than about 0.10 BTU per pound per °R. between the entropy at the maximum saturation enthalpy point on a Mollier diagram and the entropy of the saturated vapor at atmospheric pressure;

(b) utilizing the energy of the vaporized fluid to perform work, and

(c) condensing the vaporised fluid and recycling it to pass in heat exchange relationship with the heat source.

A mixture of such organic compounds may be used or there may be used a fluid comprising a major portion of a said organic compound, the fluid being itself characterised by said entropy change.

The invention further provides, in a power generating system in which a working fluid is vaporized, expanded through a machine to produce work, and cooled to a liquid state, the use as working fluid of a fluid as defined above.

It has been found that halogenated organic compounds, such as the aliphatic fluorocarbons, often lack the degree of thermal stability required of a superior Rankine cycle working fluid. Additionally, sulfur-containing organic compounds tend to be corrosive to ordinary materials of construction found in Rankine cycle equipment. Fluids with low thermal stability and high corrosion rates are not preferred as Rankine cycle working fluids, notwithstanding other advantageous properties which they might posses, such as high Rankine cycle efficiency, and accordingly, preferred fluids for use in the present invention are sulfur free and non-halogenated.

Broadly stated, the present invention employs certain organic compounds of the class defined above, preferably sulfur-free, and non-halogenated, having an entropy change of not more than 0.10 BTU per lb. per °R. between the atmospheric pressure vapor point and the maximum enthalpy point, both on the saturation curve of the Mollier diagram.

Because of the relatively low entropy change of the fluids taught by the present invention, it becomes possible to optimize the efficiency of Rankine cycle systems without the need for auxiliary equipment such as regenerators and superheaters. The working fluids characteristic of the process of the present invention offer substantial advantages, therefore, in the design of compact Rankine cycle equipment.

The description which follows refers to the accompanying drawings, in which:

Figure 1 is a diagram of a basic Rankine cycle.

Figure 2 is a Mollier diagram of 1,4-diazine, an organic compound within the scope of the class defined for use in the present invention.

Referring to FIGURE 1 of the drawing, the essential components of a basic Rankine cycle system are illustrated diagrammatically. In such a system the working fluid is pumped into heat exchange relationship with a heat source such as a boiler. The heat from the heat source vaporizes the working fluid and the vapors are then passed through a work-producing device, such as a turbine, in order to convert the energy of the expanding vapors into useful mechanical energy. The working fluid vapor is ideally expanded at constant entropy, and a portion of the available energy is converted into useful work. The function of converting heat energy into mechanical energy has been fulfilled at this point. In order to reuse the working fluid, however, the cycle is completed by further cooling the vapor which has passed through the work producing device, liquefying the vapor at constant pressure such as in a condenser, and then pumping the condensed liquid back to the boiler or heat source for reuse.

A number of variations may be made on the basic Rankine cycle system of Figure 1, all of which are well known in the art. Among these cycle variations are the regenerative cycle, the binary cycle, the saturated cycle, the superheated cycle, and the supercritical cycle. The working fluids of the classes defined for use in the present invention are adaptable to these and other Rankine-type cycles.

Application of the said working fluids in Rankine-type systems and cycles may be made for the purpose of utilizing heat energy, and particularly waste heat energy, which is available from a variety of sources which have been previously utilized as sources of heat energy for power cycles. Furthermore, because of their high thermodynamic or Rankine cycle efficiency, the said fluids are particularly advantageous for recovering and converting heat energy to mechanical energy from relatively low level heat sources. Typical heat sources which may be taken advantage of include, but are not limited to, the following: hot stack gases from industrial processes, exothermic heat from various chemical reactions, natural thermal wells, and exhaust from gas turbines and other internal combustion machines.

Some specific applications which may be cited as exemplary for use of the said working fluids: the utilization of energy from

turbine exhaust gases to drive an auxiliary turbine; the recovery of heat in chemical synthesis plants and the conversion thereof to mechanical energy to operate auxiliary equipment; the recovery of waste heat from pumps, fluid motors, turbines and expanders, which is converted to power for driving pumps, compressors, blowers, electrical generators and the like.

Referring now to FIGURE 2 of the drawing, a Mollier diagram for 1,4-diazine is presented. At the intersection of the atmospheric pressure line and the saturated vapor line, a point designated by the letter "A" is established. The maximum saturation enthalpy point on the Mollier diagram is designated by the letter "B". The change in entropy between point A and point B on the Mollier diagram of FIGURE 2 represents the basis on which the fluids of the class defined for use in the present invention are defined and limited. With reference to the relative entropy scale on the abscissa of the diagram, the approximate entropy at point A is 0.035 BTU per pound per °R. The entropy at point B is approximately 0.60 BTU per pound per °R. The entropy change from A to B, therefore, is an increase of approximately 0.025 BTU per pound per °R.

With continued reference to FIGURE 2, it is the magnitude of the entropy change which has significance herein rather than the direction of the entropy change. In the case of 1,4-diazine, the entropy change from point A to point B on the Mollier diagram is a positive quantity. For certain other compounds within the aforesaid classes the entropy change from point A to point B may be a negative quantity. Superior results are obtained for Rankine cycle use so long as the entropy change between points A and B does not exceed 0.10 BTU per pound °R., regardless of whether the entropy at point B is greater or less than that at point A.

By way of example and not in a limiting sense, the following organic compounds are representative of the fluids which can be used in the present invention having an entropy change of not more than 0.10 BTU per pound per °R. from the condition represented by point A to the condition represented by point B on the Mollier diagram: 1,3,5-triazine, 1,4-diazine, furan, cyclopentane, pyridine, pyrrole, pyrazole, imidazole, cyclopentadiene, pyrrolidine, cyclopropane, caprolactone, cyclohexane, piperidine, trimethyl triazine, benzofuran, and morpholine.

The organic working fluids for use in the present invention are cycloaliphatic, heterocyclic or fused ring organic compounds. The compounds can include, for example, alkyl, aryl, aralkyl, alkoxy, acyloxy, nitro, nitrile, amino, hydroxy, alkenyl and aryloxy substituents. In the case of the heterocyclic compounds, one or more of the hetero atoms can be nitrogen, oxygen, boron, phosphorus or silicon, or a combination of two or more of said atoms.

Illustrative of the various radicals which can appear as substituents in the aforesaid compounds are alkyl radicals, e.g. methyl, ethyl, propyl, butyl, octyl; aryl radicals, e.g., phenyl, naphthyl, tolyl, xylyl; aralkyl radicals, e.g., benzyl, phenylethyl; alkenyl radicals, e.g., vinyl, allyl; alkoxy radicals, e.g., methoxy, ethoxy, propyloxy, butoxy; acyloxy radicals, e.g., acetoxy, butoxy; aryloxy radicals, e.g., phenoxy, naphthoxy, aryloxy-substituted phenoxy, alkoxy-substituted phenoxy, alkyl-substituted phenoxy, aryl-substituted phenoxy. Other exemplary substituents are nitrile, nitro, hydroxy, amino, or multiples or combinations of these or any of the aforementioned substituents.

Where the working fluid is a fused ring organic compound it may have, for example 2 to 6 fused rings.

The organic working fluids useful in the present invention embrace a large number of chemical compounds. For illustrative purposes, some physical properties of several representative compounds are presented in Table I below:

TABLE I

Properties of Organic Working Fluids

Compound	Melting Point (°F.)	Boiling Point (°F.)	Molecular Weight	Critical Temp. (°F)	Critical Pressure (psia)	Critical Volume (ft. 3/lb.)	Entropy change from Points "A" to "B" as in Fig. 2 (BTU per lb. per °R.)
Pyridine	−44	239	79	657	817	0.05134	0.036
1,3,5-triazine	—	237	81	660	1078	0.04672	0.021
1,4-Diazine	127	244	80	668	935	0.04900	0.025
Furan	−120	88	68	422	864	0.04612	0.007
Cyclopentane	−135	121	70	461	655	0.05933	0.024
Cyclohexane	20	177	84	536	588	0.05868	0.090
Benzofuran	1	345	118	762	606	0.04637	0.081

Rankine cycle efficiencies were computed for some representative working fluids for use in the present invention in comparison with conventional fluids such as water and fluorocarbon refrigerant 12. These data are presented in Table II and the efficiencies were calculated on expansion from 500°F. to 100°F., assuming a constant turbine efficiency of 85 percent.

TABLE II

COMPOUND	*CYCLE EFFICIENCY (%)*
Flouorcarbon Refrigerant 12	15.7
Water	30.5
Pyridine	26.1
1,3,5-Triazine	26.7
1,4-Diazine	26.2
Cyclopentane	22.6
Cyclohexane	22.1

From the data of Table II it is seen that the five exemplary organic fluids of the present invention have substantially higher efficiencies than fluorocarbon refrigerant 12. Although water has a somewhat higher efficiency than the cited organic fluids, this gain is more than offset by the disadvantages caused by the deficient entropy characteristics of steam.

In addition to those sulfur-free, non-halogenated organic compounds meeting the entropy requirements established herein, it is to be understood that the method of the present invention also includes the use of mixtures or blends of one or more of said compounds wherein the entropy change of the mixture does not exceed 0.10 BTU per pound per °R. at the conditions established. Also included are mixtures wherein one or more of the included compounds has entropy characteristics outside the limits established herein but wherein the entropy change of the mixture does not exceed 0.10 BTU per pound per °R. It is to be further understood that certain additives may be added in minor amounts to the fluids of the present invention in order to obtain desired physical effects.

The working fluids defined for use in the present invention are adaptable to a variety of well known Rankine cycle systems. Further, variations may be readily devised and employed by those skilled in the art. By way of further example, a regenerative system may be employed with a supercritical cycle and binary systems may be employed with either saturated or superheated cycles, alone or in combination with a regenerative system.

WHAT WE CLAIM IS:—

1. A method of converting heat energy to mechanical energy which comprises the steps of:

(a) vaporising a fluid by passing the same in heat exchange relationship with a heat source, said fluid comprising an organic compound selected from cycloaliphatic, heterocyclic and fused ring organic compounds and characterised by an entropy change not greater than about 0.10 BTU per pound per °R. between the entropy at the maximum saturation enthalpy point on a Mollier diagram and the entropy of the saturated vapor at atmospheric pressure;

(b) utilizing the energy of the vaporized fluid to perform work, and

(c) condensing the vaporised fluid and recycling it to pass in heat exchange relationship with the heat source.

2. A method according to claim 1 wherein the said fluid is sulphur-free and non-halogenated.

3. A method according to claim 1 or 2 wherein the vaporized fluid is expanded through a turbine.

4. A method according to any of claims 1-3 wherein the compound is cycloaliphatic.

5. A method according to any of claims 1-3 wherein the compound is heterocyclic, the hetero atom or atoms being selected from nitrogen, oxygen, boron, phosphorus and silicon.

6. A method according to any of claims 1-3 wherein the compound has from 2 to 6 fused rings.

7. A method according to any of claims 4-6 wherein the compound is substituted by a substituent selected from lower alkyl, aryl, aralkyl, alkoxy, acyloxy, alkenyl, aryloxy, nitro, nitrile, amino and hydroxy.

8. A method according to any of claims 1-3 wherein the compound is pyridine.

9. A method according to any of claims 1-3 wherein the compound is 1,4-diazine.

10. A method according to any of claims 1-3 wherein the compound is 1,3,5-triazine.

11. A method according to any of claims 1-10 wherein a mixture of said organic compounds is used.

12. A method according to any of claims 1-11 wherein the fluid comprises a major portion of a said organic compound, and the fluid is itself characterised by said entropy change.

13. In a power generating system in which a working fluid is vaporized, expanded through a machine to produce work, and cooled to a liquid state, the use as working fluid of a fluid as defined in any of claims 1-10.

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1,242,935 COMPLETE SPECIFICATION
1 SHEET
This drawing is a reproduction of the Original on a reduced scale.

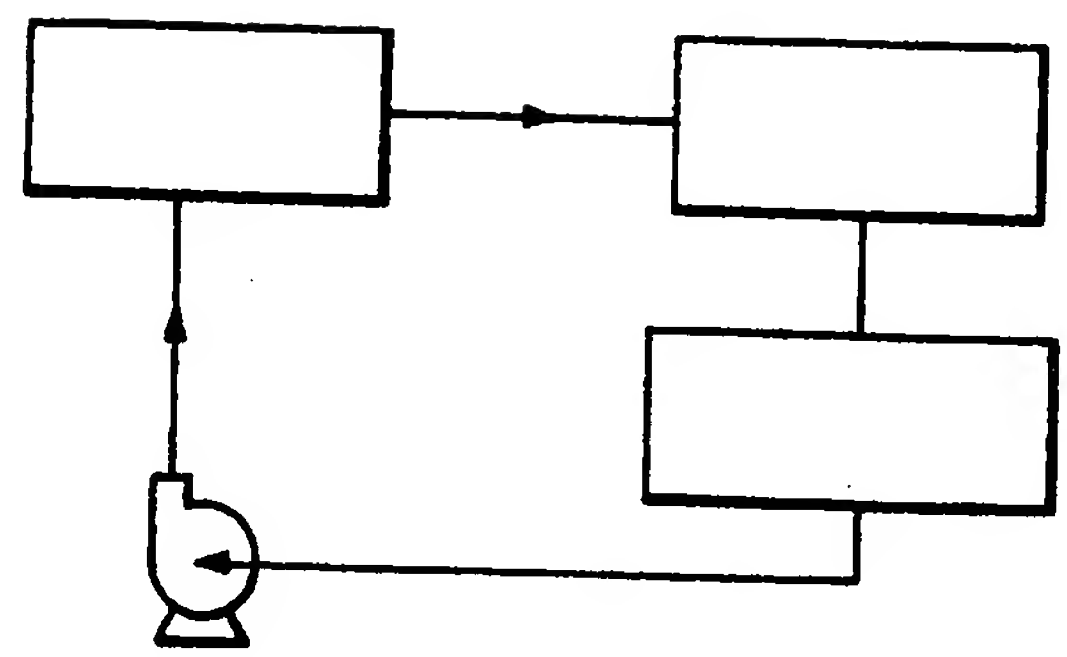

FIGURE 1

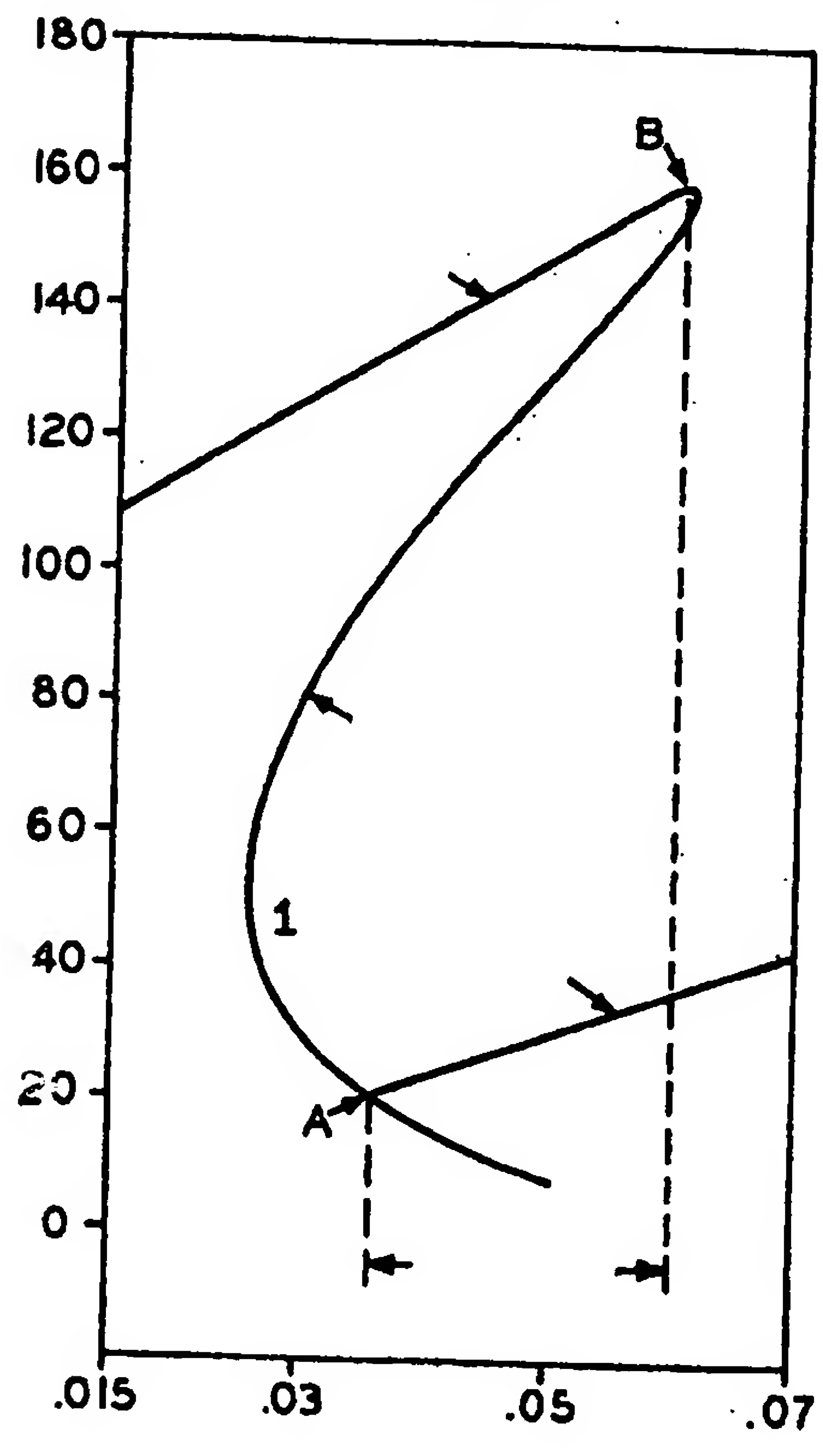

FIGURE 2